

Volatilization of Toxaphene from Lakes Michigan and Superior

RYAN R. JAMES,[†]
JEFFREY G. MCDONALD,[†]
DANIEL M. SYMONIK,[‡]
DEBORAH L. SWACKHAMER,[‡] AND
RONALD A. HITES^{*†}

Environmental Science Research Center, School of Public and Environmental Affairs and Department of Chemistry, Indiana University, Bloomington, Indiana 47405 and Environmental and Occupational Health, School of Public Health, Mayo Mail Code 807, University of Minnesota, Minneapolis, Minnesota 55455

The pesticide toxaphene was used extensively on cotton in the southern United States until its use was restricted in 1982. It was previously reported that the upper Great Lakes have received toxaphene by gas absorption following long-range transport from the south and are currently saturated with respect to toxaphene. However, the rate of loss of toxaphene from Lakes Michigan and Superior had been estimated using sparse or estimated data, and thus, these estimates had high uncertainties. For this investigation, samples were collected to provide extensive data on air, water, and sediment concentrations of toxaphene for the upper Great Lakes for the period 1997–98. These data were used to calculate the annual and seasonal fluxes of toxaphene from water to air and sediment. Lake Superior is 200–1000% saturated with toxaphene, and Lake Michigan is 200–500% saturated. It seems clear that both lakes will outgas toxaphene into the atmosphere for some considerable time in the future, and Lake Superior, because of its generally lower water temperatures and higher toxaphene concentration, will outgas toxaphene even longer than will Lake Michigan.

Introduction

Toxaphene is a broad-spectrum pesticide consisting of a complex mixture of chlorinated bornanes and camphenes. It was used extensively for the control of insects on cotton throughout the southern United States. The Hercules Company first produced toxaphene in 1947 and patented the manufacturing process in 1951 (1). First used as a piscicide during the 1950s in the upper Midwest and Canada (2, 3), over 10⁸ kg of toxaphene was eventually used in the U.S. during the next thirty years. In fact, during the 1960s and 1970s, toxaphene use was encouraged as a replacement for DDT (4). Thus, following DDT's ban in 1972 by the U.S. Environmental Protection Agency (U.S. EPA), toxaphene's use increased dramatically, and between 1966 and 1976, it was the most heavily used pesticide in the U.S. (5). The U.S. EPA severely restricted its use in 1982, citing concerns over its toxicity and environmental persistence, but limited use of existing stocks was allowed until 1986 (6). The EPA banned

all uses in 1990. Over 85% of toxaphene's use in the U.S. was in the cotton-growing states from Texas through Georgia (7), with only 1–4% of its use occurring in the upper Midwest, including the Great Lakes Basin (8).

Previous research has supported the hypothesis that toxaphene has entered the Great Lakes by atmospheric depositional processes following long range atmospheric transport from regions where it was used extensively (9). Toxaphene enters the Lakes primarily by gas absorption, rather than by dry or wet deposition, because of its higher water solubility compared to that of other organochlorine contaminants, such as PCBs. Recent work by Bidleman and colleagues revealed that ambient air concentrations in the southern states, where toxaphene was widely used, are 6–40 times higher than those over the Great Lakes (10). A study of the historical accumulation of toxaphene in Great Lakes sediments noted peak accumulations in the mid-to-late 1980s that were consistent with North American usage patterns and concluded that the observations were consistent with atmospheric deposition, with the exception of northern Lake Michigan, which may have had nonatmospheric inputs (11).

Swackhamer et al. reviewed toxaphene concentrations in Great Lakes water and biota (12). These data, and those from a study of toxaphene in fish tissue, indicate that toxaphene concentrations in Lake Superior water and biota are higher than those in the other Great Lakes (13, 14). Toxaphene concentrations in Lake Superior lake trout are of sufficient concern that fish consumption advisories have been issued by the Ontario Ministry of the Environment (15). (The Lake Michigan states do not consider toxaphene in developing their fish consumption advisories.) A dynamic model of Lakes Michigan and Superior was calibrated to existing data, and it showed that both lakes are super-saturated with respect to toxaphene (16). The higher concentration in Lake Superior, compared to those of the other Great Lakes, is caused by slower loss processes in Lake Superior. The colder summer temperatures at the air–water interface diminish volatilization, and losses to sediments are less because of slower mass sedimentation rates resulting from lower primary productivity. However, the model had considerable uncertainty due to the paucity of toxaphene data for air and sediments.

To assess the future recovery of the upper Great Lakes from toxaphene contamination, it is important to have quantitative estimates of the loss processes once the sources have been stopped. The objective of this paper is to quantify the loss rates of toxaphene from water to air and sediment for the upper Great Lakes using an extensive set of measurements of toxaphene in air, water, and sediments from 1997 to 1998. These data are also used to better understand the seasonality of the air–water exchange of toxaphene and to assess the validity of using land-based air measurements to estimate over-water fluxes.

Experimental Methods

Atmospheric Sample Collection. Air samples were collected by University of Minnesota and Indiana University personnel from U.S. EPA research vessels, the R/V *Lake Guardian* and R/V *Lake Explorer*, on transects between water sampling sites as shown in Figure 1. The over-land samples were collected at the Integrated Atmospheric Deposition Network (IADN) site located near Sleeping Bear Dunes (SBD) National Park which lies on the northeastern shore of Lake Michigan. In this case, the air sampler is about 1 km from the shore and about 15 km south of the town of Empire, MI (population 500). All air samples were collected using modified Andersen high-volume samplers (General Metal Works, model GS2310,

* Corresponding author. e-mail: hitesr@indiana.edu.

[†] Indiana University.

[‡] University of Minnesota.

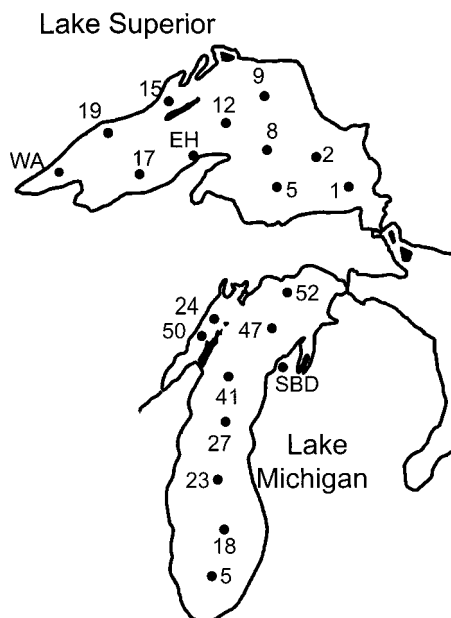


FIGURE 1. Map of Lake Superior and Lake Michigan indicating the locations of the sampling sites on and near the lakes. The numbered black circles represent the sampling sites on the lake at which the research vessels sampled air and water. WA is also a ship sampling site, EH represents Eagle Harbor, and SBD represents Sleeping Bear Dunes. The latter two sites are part of the Integrated Atmospheric Deposition Network (IADN) and are within 1 km of the lake shore.

Smyrna, GA). These samplers draw air through a filter to collect the particle-bound compounds and then through an adsorbent to collect the gas-phase compounds. Atmospheric particles were collected on quartz-fiber filters (Whatman QM-A, Clifton, NJ); atmospheric gas-phase organic compounds were collected on XAD-2 resin adsorbent (20–60 mesh, Sigma, St. Louis, MO). The sampler flow rates were calibrated before each cruise on the research vessels and quarterly at the IADN site, and the flow rates were recorded at the start and finish of each sampling period. Most of the samples were taken for 24 h, but a few were 12-h samples. A typical sample represented about 800–1000 m³ of air. Selection of the sampling dates was based on the 1997 and 1998 spring and summer cruises of the EPA research vessels. Each year included spring (unstratified) and summer (stratified) sampling dates. The over-land samples, taken at Sleeping Bear Dunes, coincided exactly with the summer 1998 cruise of the R/V *Lake Guardian* on Lake Michigan.

Water Sampling. The water and atmospheric samples were collected simultaneously aboard the same research vessels. Water was sampled using a submersible pump secured over the side of the ship at a depth of 1 m. Water was pumped through nylon tubing to the deck of the ship and then sub-sampled by a peristaltic pump, which directed the water through a glass fiber filter (Whatman) to isolate the particle phase. The filtrate was pulled by a peristaltic pump through 3 cm × 30 cm glass columns packed with XAD-2 resin (Supelco, Bellefonte, PA) to adsorb the dissolved-phase toxaphene. The sample volumes for the dissolved phase were between 75 and 150 L. The complete water sampling procedure is given elsewhere (16).

Sediment Sampling. The Lake Superior cores were collected in August of 1997 aboard the R/V *Lake Guardian*. Cores were collected at the three locations shown in Figure 1 as LS5, LS12, and LS17. A 0.084 m³ box corer was used to collect a bulk sediment sample, which was then subcored on-deck with 14-cm-diameter polycarbonate tubes. Cores were extruded under gentle nitrogen suction, to prevent

compaction, and sectioned on the ship in 0.25-cm increments for the first 3 cm, then in 1-cm increments for the remainder of the core. At locations LS12 and LS17, three subcores were obtained from each box core; at LS5 two subcores were collected. In each case, one core was used for dating purposes. The extruded samples were refrigerated on-board the ship until shipment back to the laboratory, where they were stored at 4 °C.

Sample Preparation. The analytical method for the atmospheric samples was based on those of Swackhamer et al. (17) and Glassmeyer et al. (18). Air samples were Soxhlet extracted for 24 h with 50% acetone in hexane, then solvent exchanged to hexane, and reduced in volume to about 1 mL. The primary samples and blanks were spiked with a known mass of the recovery standard, isotopically labeled ¹³C₁-chlordane (Cambridge Isotope Laboratories, Andover, MA), before extraction. Silica column chromatography was used to remove interferences from the air extracts. Disposable 13-cm Pasteur pipets plugged with glass wool were used as columns. Approximately 1 g of 3% water-deactivated silica (Davidson Chemical, Baltimore, MD) was loaded onto the columns and topped with 0.1 g of anhydrous Na₂SO₄. Three solvents in 8-mL volumes, hexane, 20% dichloromethane in hexane, and dichloromethane, were used to fractionate the samples. The last two fractions were combined, solvent-exchanged to hexane, reduced in volume to about 50 µL, and spiked with a known mass of the internal standard, 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB 204; AccuStandard Inc., New Haven, CT), prior to analysis.

The water filters and XAD-2 samples were Soxhlet extracted for 4 h with methanol, then extracted for 24 h with dichloromethane, solvent-exchanged to hexane, and reduced in volume to about 1 mL. All samples and blanks were spiked with a known mass of the ¹³C₁-chlordane recovery standard prior to extraction. These extracts were cleaned by passing them over a combined alumina (6 g of 1% deactivated, w/w) and silica gel (4.5 g of 0% deactivated, w/w) column (25 × 1.5 cm) and eluting with 150 mL of 15% dichloromethane in hexane. The complete method is given elsewhere (12).

Sediment (approximately 10 g wet) at ambient temperature was homogenized and thoroughly mixed with anhydrous Na₂SO₄ until a sand-like consistency was achieved. Samples were spiked with the recovery standard, ¹³C₁-chlordane, and Soxhlet extracted with methanol for 4 h, then extracted with dichloromethane for 20 h. The methanol fraction was mixed with 50 mL of saturated saltwater and extracted three times with hexane in a 1-L separatory funnel. The dichloromethane fraction was combined with the hexane from the methanol fraction, solvent-exchanged to hexane, and reduced in volume to about 1 mL.

Sediment sample cleanup was the same as for water extracts, with the addition of activated copper granules at the bottom of the column to remove elemental sulfur. Samples were fractionated with 50 mL of hexane, 175 mL of 15% dichloromethane in hexane, and 50 mL of 40% dichloromethane in hexane. The second fraction, which contained the toxaphene, was solvent-exchanged to hexane, reduced in volume to about 50 µL, and spiked with a known mass of the internal standard, PCB 204, prior to analysis.

Sediment Characterization. Weighing an aliquot of wet sediment and drying it to constant weight at 105 °C gave us the percent dry mass of all sediment samples. Sediment cores were dated by measuring ²¹⁰Pb activity down the cores and using the constant flux, constant sedimentation model to determine sediment accumulation rates and relative dates for each core section (19–21). Accumulations and inventories were focus-corrected based on the known deposition of ²¹⁰Pb in the Great Lakes region (22).

Analysis by Gas Chromatographic Mass Spectrometry. A Hewlett-Packard 5973 mass spectrometer, operating in the

electron-capture negative-ionization mode, was used to analyze the atmospheric and sediment samples for toxaphene. A Hewlett-Packard 5988 mass spectrometer was used for the water samples. The samples were injected into a Hewlett-Packard gas chromatograph fitted with a 60-m DB-5MS column (250- μ m i.d.; 0.25- μ m film thickness; J&W Scientific, Folsom, CA) in 2- μ L volumes using splitless mode. Helium was used as the carrier gas. The injection port temperature was maintained at 285 °C to ensure complete volatilization of the sample. The temperature program for the column began with a 1-min hold at 80 °C; it was then ramped at 10 °C/min to 210 °C, ramped at 0.8 °C/min to 250 °C, and ramped at 10 °C/min to 310 °C, where it was held for 10 min. The total run-time was 80.5 min. The GC to MS transfer line was heated to 280 °C, and the ion source of the mass spectrometer was held at 150 °C. Methane was used as the reagent gas at a manifold pressure of 2×10^{-4} Torr.

The electron-capture negative-ionization GC-MS analysis procedure was developed by Swackhamer et al. and modified slightly for subsequent use (17, 18). The M^- or $(M-Cl)^-$ ions of the hexa- to deca-chlorinated bornanes and camphenes were monitored in the selected ion-monitoring (SIM) mode. Interference ions, such as those produced by chlordane, chlordene, and ^{13}C -contributions from toxaphene fragment ions, as well as the internal standard, were also monitored. The background-subtracted, selected-ion chromatograms were integrated using a Hewlett-Packard data analysis program with a macro that generated an output file of peak areas and retention times of potential toxaphene peaks. This file was imported into a Qbasic program that selected valid toxaphene peaks based on chlorine isotope ratios and corrected for ^{13}C and other interfering compounds. Complete details are given elsewhere (18).

Because of the complex nature of the toxaphene mixture, the relative response factor (RRF) was not linear over all concentration ranges. Less abundant toxaphene congeners drop below the limit of detection as the concentration of toxaphene decreases. This phenomenon causes the RRF to vary according to a power function with respect to the total toxaphene peak area in a standard. The calculated RRFs from each standard were plotted against the total peak area for that standard. A power function was fitted to the data, from which an individual RRF for each sample was calculated based on its total toxaphene peak area.

Quality Assurance. The atmospheric and sediment samples were analyzed at Indiana University (IU), and the water samples were analyzed at the University of Minnesota (UMN). In addition, 12 duplicate sediment samples were also extracted and analyzed at UMN to ensure comparability of data. The methods of quality assurance and quality control were identical, but we will list the figures of merit separately.

All solvents were spectroscopic grade. Silica and copper were pre-extracted using dichloromethane, and the Na_2SO_4 , glass wool, and disposable pipets were heated at 450 °C overnight prior to use. A procedural blank, containing only Na_2SO_4 for the sediment samples and glass wool for the atmospheric samples, and a spike recovery sample containing toxaphene (Hercules Co.), were extracted with every batch of 5–8 samples. No toxaphene peaks were ever present in the procedural blank, and the recovery of toxaphene for the spike recovery samples was $94 \pm 20\%$ ($N = 25$) at IU and $87 \pm 19\%$ ($N = 12$) at UMN. An analytical standard of toxaphene at a concentration just above the detection limit was measured with every instrument batch to ensure adequate sensitivity. The measured mass of toxaphene in this standard (expressed as a percent of the known mass) was $103 \pm 15\%$ ($N = 27$) at IU and $100 \pm 7\%$ ($N = 28$) at UMN. The relative percent difference between duplicate samples, defined by the absolute difference between the duplicates divided by

their average, was $27 \pm 5\%$ at IU and $25 \pm 5\%$ at UMN. The average recovery was $87 \pm 17\%$ ($N = 129$) at IU and $82 \pm 13\%$ ($N = 186$) at UMN. The sample concentrations were corrected for the loss of the recovery standard.

A single primary standard of toxaphene was used to make stock solutions for both laboratories, and the diluted stock solutions were exchanged and analyzed to confirm the concentration of the other laboratory's solutions. Additionally, to ensure comparability of "real" samples between laboratories, 12 sediment extracts were analyzed first at UMN and then at IU. The average relative percent difference between the laboratories for these samples was about 17%. In addition, two sediment cores were exchanged between laboratories and analyzed separately from extraction to analysis. The difference between these cores was less than a factor of 2, which is acceptable considering the inhomogeneity of the sediment samples we exchanged and the complexity of measuring toxaphene in different laboratories. Exchanging extracts is more representative because both laboratories are analyzing the same sediment sample. The detection limits at UMN and IU were 5 ng/extract and 0.1 ng/extract, respectively. The detection limit was defined as the concentration at which we could no longer reliably measure the hexa- and deca-chlorinated homologues of toxaphene.

Results and Discussion

Atmospheric Toxaphene Concentrations. Table 1 lists the particle-bound and gas-phase concentrations of toxaphene in all of the atmospheric samples collected for this study and the dissolved phase concentration in its paired water sample. Others have shown that the gas-phase atmospheric concentration of toxaphene in the Great Lakes region is strongly temperature dependent (23–25), and the Clausius–Clapeyron equation can be used to describe this relationship (26):

$$\ln P = \frac{-\Delta H(1)}{R(T)} + \text{const} \quad (1)$$

where P is the partial pressure of the compound (in atmospheres), ΔH is a phase-transition energy, R is the gas constant, and T is temperature (in Kelvin). In this case, the ΔH value is not the enthalpy of vaporization but rather some combination of the energies associated with all of the phase changes taking place when a molecule moves from water, vegetation, or soil into the atmospheric-gas phase. In this equation, the partial pressure of toxaphene is calculated from the concentration using the ideal gas law.

The partial pressures of toxaphene versus reciprocal atmospheric temperature for each of the samples taken over the two lakes during the two years are plotted in Figure 2. The correlation between partial pressure and temperature is significant at the 99% confidence level. The energy of phase change for toxaphene can be determined from the slope of the line, and the standard error about the slope can be used to estimate its uncertainty. For toxaphene over Lake Superior and Lake Michigan (see Figure 2) this value is 76 ± 10 kJ/mol. The slopes of Clausius–Clapeyron plots are quite variable. Different values have been measured by Glassmeyer et al. at Eagle Harbor in 1997 (47 ± 22 kJ/mol) and Hoff et al. at Egbert, Ontario in 1988–1989 (91 kJ/mol) and Point Petre, Ontario in 1992 (35 kJ/mol) and 1995–1997 (44 kJ/mol) (23–25). In addition, Jantunen and Bidleman recently measured the energy for the water–air transport of toxaphene as 61 kJ/mol (27). Considering the uncertainty surrounding these numbers, our results are certainly within the expected range.

Notice that there is a high concentration outlier and a low concentration outlier near the center of Figure 2, marked A and B, respectively. The high outlier sample was taken on

TABLE 1. Particle-Bound ($C_{a,p}$) and Gas-Phase ($C_{a,g}$) Atmospheric Toxaphene Concentrations with Paired Dissolved Water ($C_{w,d}$) Toxaphene Concentrations

sample date	lake	site	$C_{a,p}$ (pg/m ³)	$C_{a,g}$ (pg/m ³)	$C_{w,d}$ (ng/L) ^a	T_a (K) ^b	T_i (K) ^c
24-Apr-97	LM	52	2.6	2.6	0.45	277	275
25-Apr-97	LM	50	ND ^d	2.7	0.28	280	275
26-Apr-97	LM	47, 41	ND	6.6	0.58	278	275
28-Apr-97	LM	27	ND	4.1	0.48	278	276
29-Apr-97	LM	23, 18	1.7	1.3	0.67	280	276
29-Apr-97	LM	23, 18	ND	4.3	0.67	280	276
2-May-97	LM	5	ND	5.2	0.67	278	276
2-May-97	LM	5	ND	4.3	0.67	278	276
3-Sep-97	LM	24	ND	2.0	0.26	287	290
3-Sep-97	LM	24	6.7	7.8	0.26	287	290
3-Sep-97	LM	52	ND	9.8	0.30	287	291
4-Sep-97	LM	50	ND	7.2	0.23	289	291
4-Sep-97	LM	50	ND	12	0.23	289	291
7-Sep-97	LM	47, 41	ND	9.7	0.33	289	290
7-Sep-97	LM	47, 41	ND	14	0.33	289	290
8-Sep-97	LM	23, 18	ND	22	0.25	290	290
8-Sep-97	LM	27	0.7	44	0.33	289	290
11-Sep-97	LM	5	0.25	5.9	0.34	289	290
28-Mar-98	LM	5	2.0	8.8	0.48	284	276
30-Mar-98	LM	18	ND	56	0.53	283	276
30-Mar-98	LM	27, 23	1.6	19	0.53	278	276
31-Mar-98	LM	47, 41	ND	5.5	0.49	277	276
2-Apr-98	LM	24, 50	ND	9.7	0.21	276	276
31-Aug-98	LM	24, 50	ND	10	0.25	293	296
31-Aug-98	LM	SBD	ND	19		289	N/A
1-Sep-98	LM	47, 41	ND	32	0.29	291	296
1-Sep-98	LM	SBD	0.7	24		290	N/A
3-Sep-98	LM	27	ND	24	0.34	293	296
3-Sep-98	LM	SBD	1.2	22		289	N/A
4-Sep-98	LM	23, 18	ND	21	0.35	295	295
4-Sep-98	LM	SBD	ND	31		291	N/A
5-Sep-98	LM	SBD	ND	71		297	N/A
5-Sep-98	LM	SBD	ND	44		297	N/A
6-May-97	LS	1, 2	5.0	3.0	1.0	277	274
6-May-97	LS	1, 2	3.8	1.9	1.0	277	274
7-May-97	LS	12, 8	ND	3.8	1.1	277	274
7-May-97	LS	12, 8	1.8	1.7	1.1	277	274
10-May-97	LS	19, 17	3.1	3.9	1.0	278	274
10-May-97	LS	19, 17	ND	3.7	1.0	278	274
14-May-97	LS	15	5.6	3.2	NS ^e	275	NS
15-May-97	LS	9	3.1	2.3	NS	275	NS
15-May-97	LS	9	4.1	2.0	NS	275	NS
25-Jul-97	LS	WA	ND	32	0.65	288	285
24-Aug-97	LS	19, 17	ND	15	0.81	289	287
24-Aug-97	LS	19, 17	ND	9.6	0.81	289	287
26-Aug-97	LS	12, 8	ND	26	1.1	289	288
26-Aug-97	LS	12, 8	ND	29	1.1	289	288
28-Aug-97	LS	1, 2	1.2	23	0.82	287	287
16-Oct-97	LS	WA	ND	ND	1.0	279	277
10-May-98	LS	19	ND	20	1.0	279	277
10-May-98	LS	19, 17	ND	19	1.0	280	277
11-May-98	LS	17	3.6	23	0.96	281	277
13-May-98	LS	12	ND	5.6	0.90	279	277
14-May-98	LS	8, 2, 1	1.4	25	0.92	280	277
17-Jun-98	LS	WA	ND	11	0.78	291	283
24-Aug-98	LS	19, 17	ND	39	0.65	293	291
25-Aug-98	LS	12	1.8	52	0.65	292	292
27-Aug-98	LS	8, 2, 1	3.4	16	0.70	294	292
21-Oct-98	LS	WA	ND	ND	0.89	279	277

^a Average concentrations at the two stations listed. ^b T_a , air temperature. ^c T_i , air-water interface temperature. ^d ND indicates a concentration of less than 0.25 pg/m³. ^e NS indicates that no paired water sample was collected.

March 30, 1998, over southern Lake Michigan and the low outlier sample was taken on September 3, 1997, over northern Lake Michigan. To investigate these two anomalies, a back-air trajectory analysis, using the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory web-based software, was performed for these two sampling

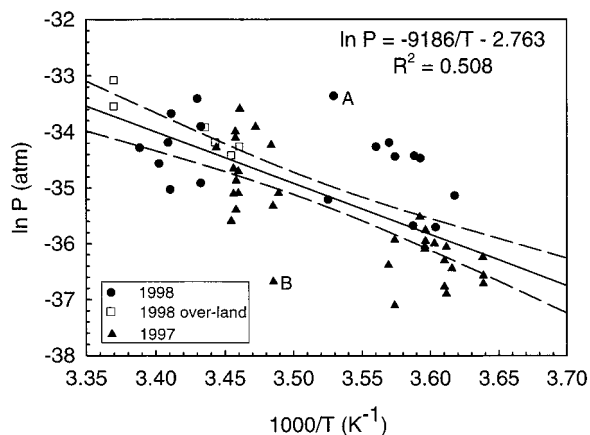


FIGURE 2. Gas-phase temperature dependence of toxaphene partial pressures including the data from 1997 and 1998 and from both lakes. Each year is represented by a different symbol, and the "over-land" samples collected at Sleeping Bear Dunes are distinguished with open squares.

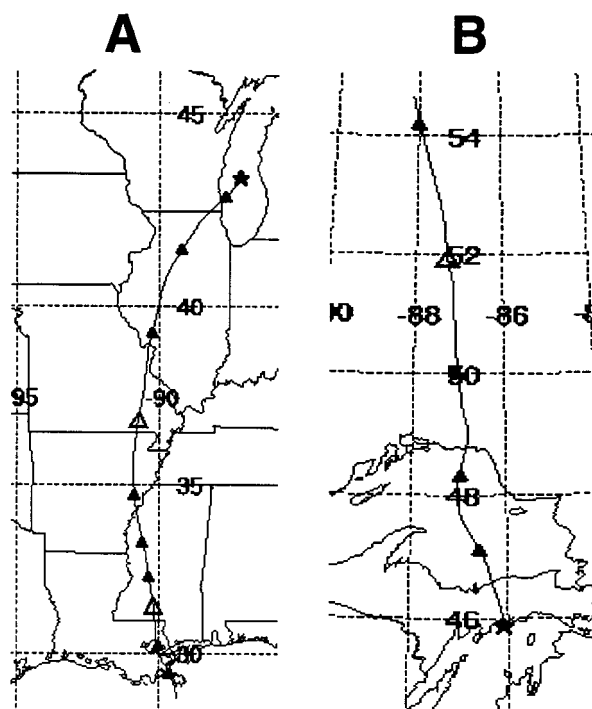


FIGURE 3. (A) Sixty-hour back trajectory for the air mass sampled on March 30, 1998, over southern Lake Michigan; and (B) 30-h back trajectory for the air mass sampled over northern Lake Michigan on September 3, 1997. The line represents the 500-m elevation (925 hPa) air mass. Starting at Lake Michigan, 24-h increments are represented by an open triangle and 6-h increments are represented by a closed triangle.

times (28). The March 30, 1998 trajectory is depicted in Figure 3A. This air mass originated at the Gulf of Mexico and traveled northward over the cotton-growing regions of Mississippi and Arkansas, where toxaphene had been applied in the past and is likely to be volatilizing from the soil into the atmosphere even now (7, 29, 30). Similar observations have led several others to suggest atmospheric transport from the southern United States as a key source of toxaphene to the Great Lakes (9, 23, 31–33). The back-trajectory for the low concentration outlier sample, collected on September 3, 1997, is depicted in Figure 3B. During this period, the air mass traveled southward from Canada where very little toxaphene was ever used. It is very reasonable that high-concentration air samples

TABLE 2. Comparison with Literature Atmospheric Total Toxaphene Concentration (in pg/m³) Ranges and Average Gas-Phase Toxaphene Concentrations ($C_{a,g}$) Adjusted to 288 K^a

source, year, and locale	range	$C_{a,g}$ @ 288 K
this study (1997–98), Lake Michigan	3–57	15 ± 4
this study (1998), Sleeping Bear Dunes, MI	19–70	n/a
this study (1997–98), Lake Superior	3–54	15 ± 4
Glassmeyer et al. (1997), Lake Superior (23)	<0.1–63	6.4 ± 2.2
Jantunen et al. (1996), Lake Superior (33)	17–41	n/a
Hoff et al. (1988–89), Egbert, ON (24)	0.1–160 ^b	16 ± 10

^a The uncertainties are estimated from the uncertainty of the slope.

^b Outlier at 580 pg/m³ omitted.

would originate over the southern U.S. and that low-concentration air samples would originate from rural Canada.

The total toxaphene concentrations (particle- plus gas-phase) over Lake Superior ranged from 3 to 54 pg/m³ with most concentrations falling between 10 and 25 pg/m³. The total toxaphene air concentrations observed over Lake Michigan ranged from 2 to 56 pg/m³, and the five over-land air samples collected at the IADN site at Sleeping Bear Dunes, MI ranged from 19 to 71 pg/m³. These concentration ranges agreed well with other over-water toxaphene air concentrations measured with similar analytical techniques. Table 2 compares the literature toxaphene concentrations to those from this study. Jantunen et al. measured a range of 17–41 pg/m³ on a cruise on Lake Superior in August of 1996, and a range of <0.1–63 pg/m³ was observed by Glassmeyer et al. at the over-land IADN site at Eagle Harbor, MI on the Keweenaw Peninsula during 1996 and 1997 (Figure 1) (23, 33). In 1988 and 1989, Hoff et al. measured the annual cycle of gas-phase concentrations of toxaphene at Egbert, in southern Ontario. They measured values as high as 160 pg/m³; however, the average concentration at 288 K (the average temperature of the Earth's atmosphere), calculated from the Clausius–Clapeyron regression, was 16 pg/m³ (24). The uncertainty of this average is dependent on the fit of the regression, which we estimate to be about 10 pg/m³. The adjusted concentration at 288 K for both lakes from this study was 15 ± 4 pg/m³, and for Glassmeyer's measurements at Eagle Harbor, the adjusted concentration was 6.4 ± 2.2 pg/m³. Although the adjusted concentration from this study is not statistically different from that of Hoff, it is significantly higher than the Eagle Harbor data (23). We suspect this difference may be magnified because our data set includes primarily spring and summer measurements. We have seen that the summer concentrations are significantly higher than those from the spring, resulting in a higher slope in the Clausius–Clapeyron regression. It seems plausible that the inclusion of concentrations across a more diverse temperature range would slightly lower the slope of the regression and lower the adjusted concentration. The difference in the maximum concentration measured in 1988/89 (160 pg/m³) and the maxima measured in more recent studies may be due to the different geographic locations of the sampling sites, differences in analytical techniques, or a decrease in atmospheric toxaphene concentrations between 1988/89 and 1997/98. In the absence of a study that monitors toxaphene over a period of many years with consistent analytical techniques, it is difficult to say whether the atmospheric concentrations of toxaphene are decreasing over time.

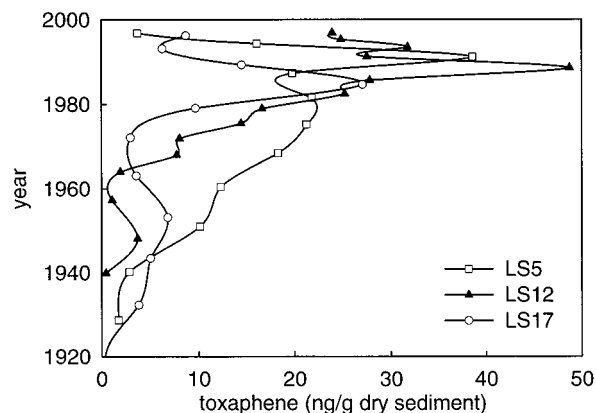


FIGURE 4. Concentrations of toxaphene in three sediment cores. The different symbols represent three different sampling locations in Lake Superior as shown in Figure 1.

However, available data indicate that water concentrations have declined significantly in Lake Superior but not in Lake Michigan during the 1990s (34).

Over-Land vs Over-Water Air Sampling. Sample collection for monitoring the atmospheric-exchange processes of persistent chemicals in the Great Lakes is expensive and inconvenient, especially if it involves a cruise on a research vessel. This task can be simplified if it is known that atmospheric samples from the shore of the lake are representative of the air over the open lake. Furthermore, this strategy allows for the collection of samples from all seasons. A study by Achman et al. demonstrated that PCB air concentrations were different from those measured over water, causing bias in flux estimates that were calculated from water and over-land air measurements (35). The data collected for this project allow for a similar comparison for toxaphene. From August 31 to September 4, 1998, four air samples were taken at Sleeping Bear Dunes, MI at exactly the same time as four air samples were collected aboard the R/V *Lake Guardian* during its cruise on northern and central Lake Michigan. The average concentration of the samples taken on shore was 24 ± 3 pg/m³, and the average concentration of those taken aboard the ship was 22 ± 5 pg/m³. Thus, near-lake measurements of atmospheric toxaphene concentrations appear to be representative of the concentrations directly above the water and can be used to accurately calculate air–water fluxes.

Sediment Toxaphene Concentrations. The historical toxaphene sediment profiles of Lake Superior are presented in Figure 4, and the maximum concentrations, accumulations, inventories, and other pertinent data are summarized in Table 3. The average maximum concentration was 39 ± 7 ng/g dry sediment, and the average maximum concentration for the Lake Superior sites occurred in 1988 ± 2 yrs. All sites show a sharp decline in concentration at approximately the time toxaphene's use was banned in the U.S. (1986), several years after toxaphene production was at its highest level (1978) (12). The average maximum accumulation for these three cores was 3.0 ± 0.9 μg/m² yr. Although there was some mixing in the upper sections of cores LS5 and LS17 (LS12 did not show mixing based on the ²¹⁰Pb data), these averages can be considered to be reasonable values for Lake Superior. These data are in good agreement with the data from the previous open lake cores from Lake Superior reported by Pearson et al. (11).

Toxaphene Composition. The toxaphene homologue profiles resembled the composition of the Hercules technical mixture in the air, water, and sediment. The sediment and water contained many more toxaphene peaks than the air, but all of the homologue compositions were largely the same.

TABLE 3. Summary of Toxaphene Sediment Data for Lake Superior^a

	LS5	LS12	LS17	average ± std. error
year sampled	1997	1997	1997	
sedimentation rate ^b (g/m ² yr)	100	160	60	110 ± 30
year of maximum accumulation	1991	1989	1985	1988 ± 2
maximum concentration (ng/g d.w.)	39	50	27	39 ± 7
present concentration (ng/g d.w.)	3.1	24	8.7	12 ± 6
focusing factor	1.52	1.70	1	—
maximum accumulation (μg/m ² yr)	2.6	4.7	1.6	3.0 ± 0.9
present accumulation (μg/m ² yr)	0.2	2.3	0.5	1.0 ± 0.6
inventory (μg/m ²)	61	66	36	54 ± 9

^a See Figure 1 for site locations; all accumulations have been corrected for focusing. ^b Determined from Pb-210 dating.

Air–Water Flux. A stagnant two-film model described in detail by Achman et al. is often used to visualize the transport of trace-level organic chemicals across the air–water interface of lakes (35, 36). Henry's law constant governs the concentration of a chemical in the water and air at the air–water interface (37). Because the resistances to mass transfer across the stagnant air and water layers combine to limit the flux of molecules across the air–water boundary, the stagnant layer with the highest resistance to mass transfer determines the total resistance to mass transfer between the bulk water and air. The toxaphene air-side resistance coefficient is much higher than the water-side resistance; therefore, the total mass transfer coefficient across the air–water interface can be approximated by just the air-side resistance (9). Equation 2 was used to calculate the instantaneous flux of toxaphene:

$$\text{Flux} = v_a(C_{a,g} - C_{w,d}H') \quad (2)$$

where v_a is the air-side mass transfer coefficient that varies

by season, as in Hoff et al. (9), $C_{a,g}$ is the atmospheric gas-phase concentration in ng/m³, $C_{w,d}$ is the dissolved water concentration in ng/m³, H' is the unitless Henry's law constant, and flux is in units of ng/m² s. The Henry's law constant for toxaphene varies with air–water interface temperature by a relationship derived from Jantunen and Bidleman (27):

$$H' = \left(\frac{1}{RT}\right) 10^{10.42 - 3209/T} \quad (3)$$

where R is 8.31 Pa m³/mol K. A negative flux value indicates a volatilization from the lake to the atmosphere.

Figure 5 illustrates that toxaphene is volatilizing out of Lakes Superior and Michigan during the spring and summer of 1997 and 1998. The volatilization magnitudes range from about 250 to 3000 ng/m²·season, where "season" consists of 3-month periods beginning with the month of March and extending through May for the spring and from June through September for the summer. These are the paired air–water fluxes averaged over each season. Both lakes experience a decrease in volatilization during the spring of 1998 compared with the spring of 1997 because of the high gas-phase concentrations during the spring of 1997 were 4 and 3 pg/m³ for Lake Michigan and Lake Superior, respectively, compared with 10 and 20 pg/m³ in 1998. The higher concentration shifted the concentration gradient slightly toward the water and thus decreased the volatilization during the spring. The fluxes out of Lakes Superior and Michigan were constant throughout the spring and summer of 1997, but the magnitude of the fluxes increased significantly from the spring to the summer of 1998. This is due to the significantly warmer temperatures in both lakes in 1998 compared to those in 1997 and the dependence of Henry's constant on temperature (38). The magnitude of toxaphene volatilization in 1997 and 1998 is similar to what Hoff et al. estimated for toxaphene in the early 1990s (9). Additionally, the behavior of toxaphene in 1998 is similar to the behavior of PCBs in Lake Superior as observed by Hornbuckle et al. from 1988 to 1992, when there was a strong seasonal/temperature dependence on the air–water flux (39).

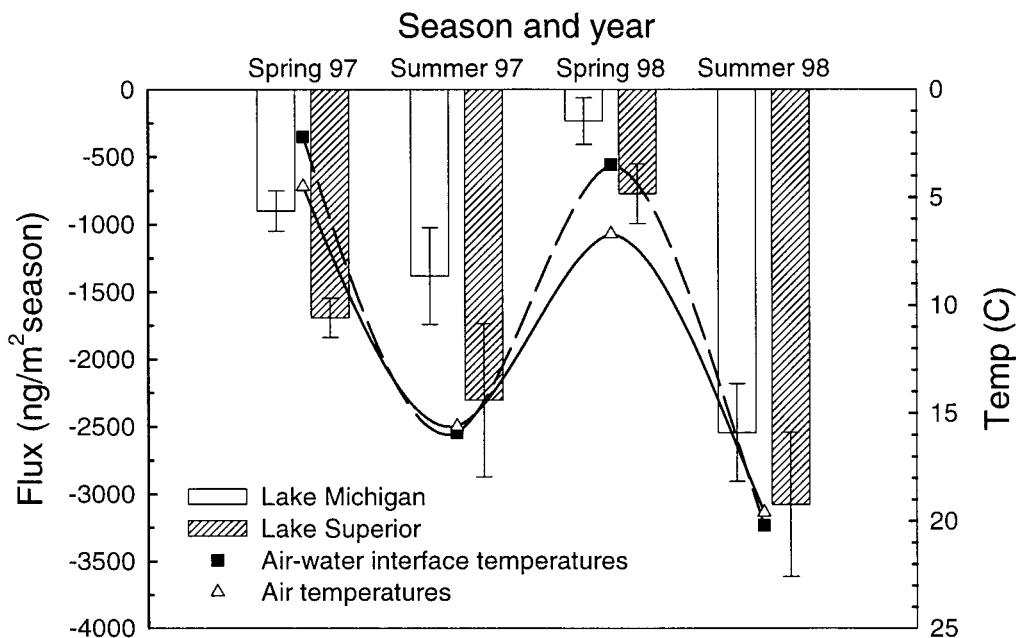


FIGURE 5. Air–water fluxes out of Lake Michigan and Lake Superior during the spring and summer of 1997 and 1998. The average atmospheric and air–water interface temperatures over the same time periods are superimposed on the chart. The error bars represent one standard error.

Swackhamer et al. estimated a net volatilization from Lake Superior and a small net load from the atmosphere into Lake Michigan for 1993–1996 (16). This is similar in magnitude to our results but different in direction for Lake Michigan. Our measurements show that Lake Superior has a larger volatilization flux than Lake Michigan, which also undergoes net volatilization. It seems likely that the differences are due to differences in the estimated summertime atmospheric toxaphene concentrations, which Swackhamer et al. found to be about 60 pg/m³ but we found to be about 25 pg/m³. The higher atmospheric concentration leads to an underestimate of the volatilization flux from both of the lakes during the summer, when the largest differences between the studies occurred. Also, Swackhamer et al. (16) used seasonal average temperatures and fixed seasonal *H'* values, whereas we used actual temperature data and *H'* adjusted for the temperature at each individual sampling time. Of course, Swackhamer et al. were attempting to estimate the transport for 1993–96, not 1997–98.

More toxaphene is volatilizing out of Lake Superior than Lake Michigan during the spring of each year. Even though springtime air–water interface temperatures are similar in each lake, the higher water concentration of toxaphene in Lake Superior (1 ng/L, compared to 0.5 ng/L in Lake Michigan) drives the flux. However, during the summer, the much higher temperatures increase the effect of Henry's law constant on the flux, and we observe similar magnitudes of volatilization out of the two lakes.

Seasonal transitions involving larger than normal temperature fluctuations seem to exhibit dramatic changes in air–water exchange processes. This effect is shown in the summer of 1998 when the magnitude of flux from both lakes increased dramatically after the spring. The flux from Lake Michigan increased from 240 to 2500 ng/m²-season when the average temperature during the summer was 19 °C higher than during the spring. The flux from Lake Superior increased from 770 to 3100 ng/m²-season when the average temperature during the summer was 15 °C warmer than during the spring. This stands in contrast to 1997 when seasonal fluxes did not change significantly from spring to summer of 1997, when the average seasonal temperature change from the spring to the summer of Lake Michigan was 4 °C smaller and in Lake Superior 3 °C smaller than in 1998. This may indicate that a small but critical temperature change between seasons triggers a large volatilization from the lakes. Smaller temperature changes between seasons may hold the flux constant, whereas large temperature changes increase volatilization.

Present Losses of Toxaphene from Lake Superior and Lake Michigan. We have shown that toxaphene was volatilizing out of Lake Superior and Lake Michigan during the spring and summer of 1997 and 1998. This indicates that the water in each of these lakes is over-saturated with toxaphene. Lake Michigan is 200–500% saturated and Lake Superior is 200–1000% saturated during the spring and summer. Lake Superior is about 300% saturated during the fall with a volatilization flux of about 3000 ng/m²-season. Data from Lake Michigan from 1995 indicate that the winter concentrations are very similar to spring concentrations (Swackhamer, unpublished data). This estimate shows that, even in the winter, both lakes would be 500–3000% saturated, corresponding to a volatilization flux out of both lakes between 1000 and 3000 ng/m²-season. It seems clear that both lakes will outgas toxaphene into the atmosphere for some considerable time into the future and that Lake Superior, because of its generally lower water temperature and higher toxaphene concentrations, will outgas toxaphene even longer than will Lake Michigan.

Acknowledgments

The authors thank the captain and crew of the U.S. EPA research vessels *Lake Guardian* and *Lake Explorer*: Jib Baker, Susan Glassmeyer, Amy Heitala, Annette Trowbridge, Anne Lutz, and Matt Wogan, for assistance in air, water, and sediment sampling. We thank Daniel Engstrom of the Minnesota Science Museum St. Croix Watershed Research Station for the sediment dating. The U.S. EPA (Grant No. R825246) supported this work.

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Received for review December 12, 2000. Revised manuscript received May 25, 2001. Accepted June 13, 2001.

ES0019631